

ELECTROLYTIC NONSTOICHIOMETRIC MOLYBDENUM OXIDES IN LITHIUM BATTERIES

*E.Shembel**, *R.Apostolova***, *V.Nagirny***,
*M.Chuiko***, *Ph.Grebenkin***, *P.Novak** and
*P.Lytvyn****

**Ener1, Via Fontevivo, 25, 19125, LaSpezia, Italy*
e-mail: eshembel@ener1.com, pnovak@ener1.com

***Ukrainian State Chemical Technology University,*
8 Gagarin Ave., 49005, Dnepropetrovsk, Ukraine
e-mail: shembel@onil.dp.ua

****Institute of Semiconductors Physics, 45 Nauki Ave.,*
252650, Kiev, Ukraine,
e-mail: plyt@isp.kiev.ua

Electrolytic production of metal oxides in thin layers is feasible for the realization of the film lithium batteries. Synthesis of the ballast-free electrodes based on molybdenum oxides has been carried out by using the cathodic reduction of acid ammonium-, sodium-molybdate solutions [1].

Specific discharge characteristics and the reserves of molybdenum oxides in lithium batteries are known to be the function of the oxide stoichiometry. Electrolysis enables the production of the wide spectrum of molybdenum oxide compositions.

We have established that the surface morphology of electrolytic deposits of molybdenum oxides depends on the electrolyte composition and changes gradually, as annealing temperature (T°) of the deposits rises, from grained ($T_{\text{anneal}}=18^\circ\text{C}$) and coarse-grained ($T_{\text{anneal}}=450^\circ\text{C}$) to block one ($T_{\text{anneal}}=650^\circ\text{C}$) -Figs.1-3.

The lateral sizes of grains, determined by AFM, range from 7 to 25 nm (18°C) – Fig. 1. The blocks being layered formations, are the linear sizes ranging from 200 to 1500 nm (600°C - Fig. 3).

Under the ranging of electrolyte composition and the annealing conditions of electrolytic deposits the molybdenum oxides have been produced with the structure corresponding to the following compositions: MoO_3 , Mo_9O_{26} , Mo_8O_{23} , Mo_4O_{11} . Crystallite sizes in the deposits, calculated according to X-ray patterns data are within the range of 12 – 68 nm.

According to the results of thermal and X-ray analysis, the molybdenum oxide synthesized from sodium molybdate electrolyte, corresponds to the formula $\text{MoO}_x.\text{nH}_2\text{O}$ ($x=2.75-2.88$, $n=1.33-1.35$). $\text{Mo}_4\text{O}_{11}.\text{nH}_2\text{O}$. $y.\text{NH}_3$ oxide composition obtained from ammonium electrolyte have been determined. Ammonium ions availability in electrolytic deposit has been confirmed by absorption IR spectroscopy.

Electrochemical intercalation of lithium ions in molybdenum oxides was investigated in compact thin-layer deposits on a stainless steel and in composite spread electrodes based on finely divided oxide powder with the additives of black and PTFE binder. Electrolyte: PC, DME, 1M LiClO_4 .

The molybdenum oxides were tested as a cathode material and also in anodes of lithium-ion battery with LiCoO_2 cathode. The primary discharge capacity of molybdenum oxides increased with the rising of deposits' annealing temperature, whereas coulombic cycling efficiency decreases. The initial discharge capacity of cathode in power sources 2325 of $\text{Mo}_4\text{O}_{11}/\text{Li}$ system is more than 300 mAhg^{-1} at the discharge up to 1.5 V ($I_{\text{disch}}=0.2 \text{ mAcm}^{-2}$). Reversible capacity became stable at the level $170-200 \text{ mAhg}^{-1}$. Electrolytic Mo_9O_{26} oxide as an anode material in lithium-ion battery gave off 150 mAhg^{-1} during the 1st and the 6th cycles within the voltage range 3.0-1.1 V. Cycling is in progress.

References

1. V.M.Nagirny, R.D.Apostolova, A.S.Baskevich, E.M.Shembel // Journal of Applied Chemistry, 73 (2000) 406. In Russian.

AFM images of electrolytic Mo – oxides.

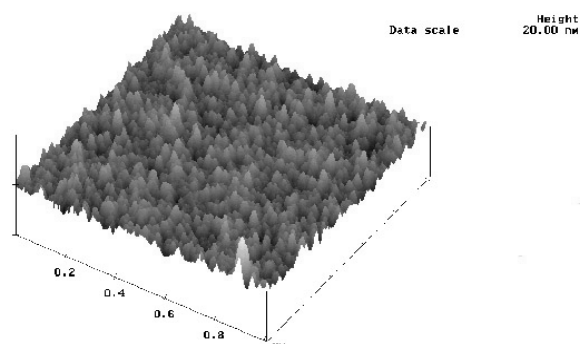


Fig. 1 – Temperature treatment 18°C ,

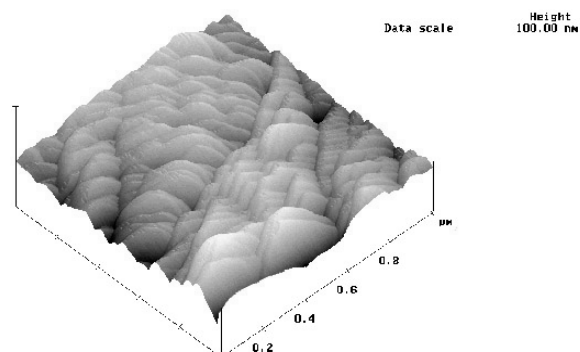


Fig. 2 – Temperature treatment 450°C (15 min),

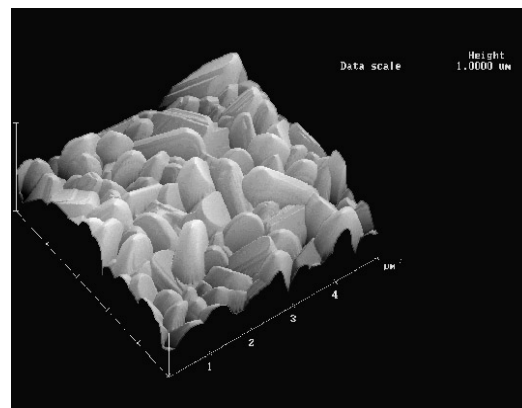


Fig. 3 – Temperature treatment 600°C (5 min).